POROUS ELECTRODE AND ITS MANUFACTURE

Publication number: JP10106347
Publication date: 1998-04-24
Inventor: SASAKI KAZUYA
Applicant: TANAKA PRECIOUS METAL IND
Classification:
- international: ***C04B38/00; H01B1/16;*** **C04B38/00; H01B1/14;** (IPC1-7): H01B1/16; C04B38/00
- European:
Application number: JP19960280156 19960930
Priority number(s): JP19960280156 19960930

Abstract of **JP10106347**

PROBLEM TO BE SOLVED: To provide a thin porous electrode having uniform, continuous pores. SOLUTION: Platinum group metal powder and ceramic powder both having different pore size and a particle size of 1&mu m or less are mixed and dispersed each other, then dispersed in vehicle to prepare paste, the paste is applied to a substrate, and they are baked to obtain a porous electrode. In order to mix and disperse the powder, a dry ball mill method is the most suitable, but an ultrasonic vibration method or joint use of the ultrasonic vibration method and dry ball mill method can be used.

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平10－106347

(43)公開日　平成10年(1998)４月24日

(51)Int.Cl.[6]	識別記号	ＦＩ	
Ｈ０１Ｂ　1/16		Ｈ０１Ｂ　1/16	Ａ
Ｃ０４Ｂ　38/00	３０３	Ｃ０４Ｂ　38/00	３０３Ｚ

審査請求　未請求　請求項の数13　ＦＤ　（全　４　頁）

(21)出願番号　特願平8－280156

(22)出願日　平成８年(1996)９月30日

(71)出願人　000217228
田中貴金属工業株式会社
東京都中央区日本橋茅場町２丁目６番６号

(72)発明者　佐々木一哉
神奈川県厚木市飯山字台の岡2453番21号
田中貴金属インターナショナル株式会社厚木工場内

(54)【発明の名称】　多孔質電極及びその製造方法

(57)【要約】

【目的】　薄くて均質な連続気孔性の多孔質電極を提供しようとするものである。

【構成】　相互に粒径が異なり、粒径が１μｍ以下の白金族金属粉末とセラミック粉末とを、あらかじめ混合分散させて、両者が対状に分散する様になし、これをビヒクルに分散させたペーストを、基材上に施して焼成することにより、多孔質電極を得る。粉末の混合分散には、乾式ボールミルが最適であり、超音波振動法、或いは超音波振動法と乾式ボールミルと併用でも行うことができる。

【特許請求の範囲】
【請求項１】　粒径が１μｍ以下の白金族金属粉末と、粒径が１μｍ以下で前記白金族金属粉末とは粒径の異なるセラミック粉末とを混合分散させたものを、ビヒクル中に分散させてなるペーストを基材に施して焼成してなる多孔質電極。
【請求項２】　白金族金属粉末は、白金粉末である「請求項１」の多孔質電極。
【請求項３】　白金族金属粉末は、白金ロジウム合金粉末である「請求項１」の多孔質電極。
【請求項４】　セラミック粉末は、白金族金属粉末の１５重量パーセント以下である「請求項１」の多孔質電極。
【請求項５】　セラミック粉末は、ガス透過性セラミック粉末である「請求項１」の多孔質電極。
【請求項６】　ガス透過性セラミック粉末は、ジルコニア粉末である「請求項５」の多孔質電極。
【請求項７】　ガス透過性セラミック粉末は、ジルコニア粉末の一部を酸素透過度を増すように改質した改質ジルコニア粉末である「請求項５」の多孔質電極。
【請求項８】　白金族金属粉末とセラミック粉末との双方の粒子径が０．１μｍ以下である「請求項１」から「請求項７」のいずれかの多孔質電極。
【請求項９】　白金族金属粉末とセラミック粉末とを乾式ボールミルにより混合分散させてからビヒクル中に分散させてペーストを得、しかる後に前記ペーストを基材上に施して焼成する多孔質電極の製造方法。
【請求項１０】　白金族金属微粉末とセラミック微粉末とを水中で超音波混合分散させてから乾燥してビヒクル中に分散させてペーストを得、しかる後に前記ペーストを基材上に施して焼成する多孔質電極の製造方法。
【請求項１１】　白金族金属微粉末とセラミック微粉末とを水中で超音波混合分散させて乾燥してから乾式ボールミルにより再混合分散させたものをビヒクル中に分散させてペーストを得、しかる後に前記ペーストを基材上に施して焼成する多孔質電極の製造方法。
【請求項１２】　基材はグリーンシートよりなり、基材と多孔質電極とが同時に焼成されることを特徴とする「請求項９」から「請求項１１」のいずれかの多孔質電極の製造方法。
【請求項１３】　グリーンシートは、イオン伝導性固体電解質物質からなることを特徴とする「請求項１２」の多孔質電極の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】この発明は、燃料電池その他に用いて好適な、応答速度の速い多孔質電極及びその製造方法に関する。
【０００２】
【従来の技術】一般に、導体ペーストは、粒径が１２μｍ前後の金属粉体をビヒクル中に分散させてなるものであるので、多孔質電極を形成しようとすると１０μｍを超える厚さとなるばかりか、均質な連続多孔性となりにくく、応答性の極めて悪いものとなった。
【０００３】
【発明が解決しようとする課題】そのため、応答性の良い薄い電極を得るべく、ペーストをうらごしして小粒径のペーストとして、薄く塗布して焼成すると、電極は連続性を失い、電気的導通が無くなってしまった。特に電極の耐久性を増すために１５００℃程度で焼成した場合には、その度合いが大きくなってしまう。そこでこの発明は、薄く均質な連続気孔性の多孔質電極を提供することを目的とする。
【０００４】
【課題を解決するための手段】この発明の目的は、粒径が１μｍ以下の白金族金属粉末と、粒径が１μｍ以下で前記白金族金属粉末とは粒径の異なるセラミック粉末とを混合分散させたものを、ビヒクル中に分散させてなるペーストを印刷や塗布等の手段により基材に施して焼成してなる多孔質電極によって達成される。この発明の目的は、白金族金属粉末は、白金粉末である「請求項１」の多孔質電極によって達成される。この発明の目的は、白金族金属粉末は、白金ロジウム合金粉末である「請求項１」の多孔質電極によって達成される。この発明の目的は、セラミック粉末は、白金族金属粉末の１５重量パーセント以下である「請求項１」の多孔質電極によって達成される。この発明の目的は、セラミック粉末は、ガス透過性セラミック粉末である「請求項１」の多孔質電極によって達成される。この発明の目的は、ガス透過性セラミック粉末は、ジルコニア粉末である「請求項５」の多孔質電極、或いは、ガス透過性セラミック粉末は、ジルコニア粉末の一部を酸素透過度を増すように改質した改質ジルコニア粉末である「請求項５」の多孔質電極によって達成される。この発明の目的は、白金族金属粉末とセラミック粉末との双方の粒子径が０．１μｍ以下である「請求項１」から「請求項７」のいずれかの多孔質電極によって達成される。更に、この発明の目的は、白金族金属粉末とセラミック粉末とを乾式ボールミルにより混合分散させてからビヒクル中に分散させてペーストを得、しかる後に前記ペーストを基材上に施して焼成する多孔質電極の製造方法、或いは、白金族金属微粉末とセラミック微粉末とを水中で超音波混合分散させてから乾燥してビヒクル中に分散させてペーストを得、しかる後に前記ペーストを基材上に施して焼成する多孔質電極の製造方法、または、白金族金属微粉末とセラミック微粉末とを水中で超音波混合分散させて乾燥してから乾式ボールミルにより再混合分散させたものをビヒクル中に分散させてペーストを得、しかる後に前記ペーストを基材上に施して焼成する多孔質電極の製造方法によって達成される。また、この発明の目的は、基材はグリーン

シートよりなり、基材と多孔質電極とが同時に焼成されることを特徴とする「請求項９」から「請求項１１」のいずれかの多孔質電極の製造方法、或いは、グリーンシートは、イオン伝導性固体電解質物質からなることを特徴とする「請求項１２」の多孔質電極の製造方法によって達成される。

【０００６】

【発明の実施の形態】この発明によれば、白金族金属粉末とセラミック粉末との粒子径を１μｍ以下とすることにより、３μｍ程度の薄い電極を形成できる。また、白金族金属粉末とセラミック粉末との粒径を異ならせて混合分散させる事により、異なる粒径の粒子が表面自由エネルギーを小さくするように結合するため、白金族金属粉末粒子とセラミック粉末粒子とが必ず対を成す状態に分散し、焼結状態では均質な連続気孔性の多孔質電極を形成する。この際、セラミック粉末を、白金族金属粉末の１５重量パーセント以下とすると多孔質電極の導電性を維持できる。白金族金属粉末として、白金粉末、或いは白金ロジウム合金粉末を用いれば、材料のガス安定性が良く、比較的低融点であるので、多孔質電極を形成する際の焼成作業が比較的に簡単になる。更に、多孔質電極の一部を形成するセラミック粉末をガス透過性セラミック粉末、例えば酸素透過性のジルコニア粉末等とすれば、燃料電池の燃料ガス等との反応の良い電極となり、白金族金属粉末とセラミック粉末との粒径を０．１μｍ以下とすれば、電極厚が薄くなり、電極の応答速度が格段に向上する。

【０００７】粒径の異なる白金族金属粉末と、セラミック粉末とを、共に乾式ボールミル内で混合分散させる事により、両粉末にメカノケミカル的効果が加えられ、それぞれ粒径の異なる白金族金属粉末とセラミック粉末とが対状に分散する。材料が微粉末の場合は、超音波により、好適に混合分散させることができる。基材としてグリーンシートを用いれば、任意の形状の多孔質電極を提供でき、更に、イオン伝導性のグリーンシートとすれば、基材部分をもガス透過性とすることができる。

【０００８】

【実施例１】平均粒径０．０５μｍの白金粉末を１００重量部と、平均粒径が０．１６μｍで、カルシウム処理かイットリウム処理して酸素透過度を増す様に改質したジルコニア粉末を１０重量部とを遊星型ボールミルに投入して６時間乾式混合分散させた。ここで得られた混合分散粉末を、樹脂、溶剤、界面活性剤等からなるビヒクル中に分散させてペーストを得た。この様に、粒径の異なる白金族金属粉末（白金粉末）とセラミック粉末（ジルコニア粉末）とを、予めボールミルで混合させる事により、粒径の異なる粒子が表面エネルギーを小さくする様に結合しあい、更にボールの衝突による物理的力が加わり、更にメカノケミカル効果も加わるため、粒径の異なる粉末同志が結合しあった状態で分散する。即ち、粒径が異なるため、白金族金属粉末同志、或いはセラミック粉末同志が凝集してしまう事が無くなる。その結果、ペースト中においても、白金族金属粉末とセラミック粉末とは必ず隣接し合った状態で分散していることになる。かくして得られたペーストを、イオン伝導性固体電解質物質からなるグリーンシート上に施して１５００℃で焼成することにより、厚さ１．８μｍの多孔質電極を得た。この多孔質電極の評価に当たり、応答速度は、交流インピーダンス測定により知る事ができ、交流インピーダンス測定により得られる抵抗値Ｒと、キャパシタンスＣとの積（ＲｘＣ＝時定数）が、応答時間と正の相関がある。又、導体抵抗値は、四探針法等により評価することができる。そこで、６００℃の酸素気流中に多孔質電極を置き、０．０１ボルトの電圧を印加してインピーダンス測定を行った所、時定数は０．０４３秒であった。また、導体抵抗値は、４１８ｍΩ／□であった。尚、得られた多孔質電極は、完全な連続気孔性であった。

【０００９】

【実施例２】平均粒径０．０５μｍの白金粉末１００重量部と、平均粒径０．１μｍのジルコニア粉末１０重量部とを遊星型ボールミルに投入して６時間乾式混合分散させた後、ビヒクル中に分散させてペーストを得た。このペーストをイオン伝導性固体電解質物質からなるグリーンシート上に施して１５００℃で焼成することにより、厚さ１．６μｍの多孔質電極を得た。得られた多孔質電極は、完全な連続気孔性であり、時定数は０．０１５秒、導体抵抗値は２２０ｍΩ／□であった。

【００１０】

【実施例３】平均粒径０．０５μｍの白金粉末１００重量部と、平均粒径０．３５μｍのジルコニア粉末１０重量部とを遊星型ボールミルに投入して６時間乾式混合分散させた後にビヒクル中に分散させてペーストを得た。得られたペーストを基材上に塗布して施し、１５００℃で焼成して、厚さ２．０μｍの多孔質電極を得た。評価の結果、この多孔質電極は、完全な連続気孔性であり、時定数は０．０３０秒、導体抵抗値は１８０ｍΩ／□であった。

【００１１】

【実施例４】平均粒径０．０５μｍの白金粉末１００重量部と、平均粒径０．０２μｍのジルコニア粉末１０重量部とを水槽内に投入し、この水槽内に超音波振動を与えて両粉末を混合分散させてから、この分散粉末を適当な通過孔径の網等によりすくい上げて乾燥させ、白金粉末とジルコニア粉末とが均等分散した乾燥分散粉末をビヒクル中に分散させてペーストを得た。得られたペーストを、未焼成陶紙であるグリーンシート上に施してから、両者を１５００℃で焼成し、基材を形成する焼成陶紙上に厚さ２．０μｍの多孔質電極を作製した。超音波振動により高度に分散された白金粉末とジルコニア粉末

とは、評価の結果、焼成によって完全な連続気孔性の多孔質電極を形成し、時定数は０．０５秒、導体抵抗値は３９０mΩ／□であった。

【００１２】

【実施例５】平均粒径０．０５μmの白金粉末１００重量部と、平均粒径０．０２μmのジルコニア粉末１０重量部とを、水中で超音波振動を加えて混合分散させた後に水中から引き上げて乾燥させ、この乾燥分散粉末を遊星型ボールミルにより６時間乾式混合分散させた。その後、この乾式再混合分散粉末をビヒクル中に分散させてペーストを得た。得られたペーストを、イオン伝導性固体電解質物質よりなるグリーンシート上に施して、両者を１５００℃で焼成した。これにより、基材を形成する焼成陶紙上に厚さ１．６μmの多孔質電極を作製した。評価の結果、得られた多孔質電極はきめこまかい連続気孔を持っており、時定数は０．０２秒、導体抵抗値は１５０mΩ／□であった。

【００１３】

【比較例１】平均粒径１．０μmの白金粉末１００重量部と、平均粒径０．１４μmのジルコニア粉末１０重量部とを、ビヒクル中に分散させて得たペーストを、基材上に塗布して施してから１５００℃で焼成して厚さ３．０μmの多孔質電極を作製した所、多孔質電極は所所で分断して連続性を失い、電気的導通は得られなかった。これは、本発明の様に、白金粉末とジルコニア粉末とをあらかじめ混合分散させて、白金粉末とジルコニア粉末とが必ず対を成すように分散させなかった為、白金粉末同志の凝集部分、或いはジルコニア粉末同志の凝集部分が点在した為である。

【００１４】

【比較例２】平均粒径０．０５μmの白金粉末１００重量部と、平均粒径０．１４μmのジルコニア粉末とを遊星型ボールミルに投入して６時間乾式混合分散させ、この混合分散粉末をビヒクル中に分散させてペーストを得た。得られたペーストを基材上に塗布して施し、これを１５００℃で焼成して４．０μm厚の多孔質電極を作製した。しかしながら、連続気孔性の多孔質電極形状は得られたものの、ジルコニア粉末の含有量が多すぎて、白金粒子同志の連続接触が得られなかった為、電気的導通は得られなかった。

【００１５】尚、上記の例に於いては、白金族金属粉末の例として、白金粉末の例を示したが、そのほかに、ルテニウム、ロジウム、パラジウム、オスミウム、イリジウム等の粉末、或いは白金ロジウム合金等の合金粉末を用いることができる。また、ガス透過性のセラミックとして、酸素透過性のジルコニア粉末の例を示したが、酸素透過性のセラミックとしてはこの他に、アルミナやセリウムなどの酸化物セラミックスを用いることができる。勿論、用途によっては、水素透過性セラミックや窒素透過性のセラミック等を用いることができる。更に、超音波混合分散方式による製造方法は微粉末の混合分散に適してはいるが、振動停止後の微粉末の沈降による悪影響等を補償するためには、粉末乾燥後に再度乾式ボールミルによる混合分散を繰り返すことができる。

【００１６】

【発明の効果】上記の通り、この発明によれば、厚さ３μm以下の連続気孔性多孔質電極を再現性良く得ることができ、応答時間が短く、導体抵抗値が小さいばかりか、連続気孔性の多孔質体であるため熱応力に対して破損しにくく耐久性の高い電極を提供できるものとなる。更にこの発明によれば、導体として白金族金属粉末を用いているので、化学的安定性が強く、寿命の長い電極となる他、セラミックとして、各種のガス（又は燃料流体）と非性又は親和性が有るガス透過性の材料を用いることができるので、各種の用途に応じた電極を提供でき、また、白金族金属粉末とセラミック粉末との粒径を０．１μm以下とすれば、応答時間を大幅に短縮できる等の利点も得られる。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-106347

(43)Date of publication of application : 24.04.1998

(51)Int.Cl. H01B 1/16
C04B 38/00

(21)Application number : 08-280156

(22)Date of filing : 30.09.1996

(71)Applicant : TANAKA KIKINZOKU KOGYO KK

(72)Inventor : SASAKI KAZUYA

(54) POROUS ELECTRODE AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thin porous electrode having uniform, continuous pores.

SOLUTION: Platinum group metal powder and ceramic powder both having different pore size and a particle size of 1μm or less are mixed and dispersed each other, then dispersed in vehicle to prepare paste, the paste is applied to a substrate, and they are baked to obtain a porous electrode. In order to mix and disperse the powder, a dry ball mill method is the most suitable, but an ultrasonic vibration method or joint use of the ultrasonic vibration method and dry ball mill method can be used.

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]A porous electrode in which particle diameter gives a paste in which it makes it come to distribute in a vehicle that to which mixture dispersion of the end of ceramic powder particle diameter differs between platinum metal powder of 1 micrometer or less and particle diameter by 1 micrometer or less as for said platinum metal powder was carried out to a substrate, and calcinates it.
[Claim 2]A porous electrode of "claim 1" whose platinum metal powder is platinum powder.
[Claim 3]A porous electrode of "claim 1" whose platinum metal powder is platinum-rhodium alloy powder.
[Claim 4]A porous electrode of "claim 1" which is 15 or less mass percents of platinum metal powder the end of ceramic powder.
[Claim 5]A porous electrode of "claim 1" which it is in the end of gas permeation nature ceramic powder the end of ceramic powder.
[Claim 6]A porous electrode of "claim 5" which is zirconia powder the end of gas permeation nature ceramic powder.
[Claim 7]A porous electrode of "claim 5" which is the refining zirconia powder which reformed some zirconia powder the end of gas permeation nature ceramic powder so that oxygen transmittance might be increased.
[Claim 8]One porous electrode of "claim 1" to "claims 7" whose particle diameter of both sides of platinum metal powder and the end of ceramic powder is 0.1 micrometer or less.
[Claim 9]A manufacturing method of a porous electrode which makes it distribute in a vehicle, obtains a paste since mixture dispersion of platinum metal powder and the end of ceramic powder is carried out with a dry type ball mill, gives said paste on a substrate and calcinates it after an appropriate time.
[Claim 10]A manufacturing method of a porous electrode which dries since ultrasonic mixture

dispersion of platinum metal impalpable powder and the ceramic impalpable powder is carried out underwater, makes it distribute in a vehicle, obtains a paste, gives said paste on a substrate and calcinates it after an appropriate time.

[Claim 11]A manufacturing method of a porous electrode which distributes in a vehicle what carried out re-mixture dispersion with a dry type ball mill, obtains a paste after carrying out ultrasonic mixture dispersion of platinum metal impalpable powder and the ceramic impalpable powder underwater and drying, gives said paste on a substrate and calcinates it after an appropriate time.

[Claim 12]A manufacturing method of one porous electrode of "claim 9" to "claims 11", wherein a substrate consists of green sheets and a substrate and a porous electrode are calcinated simultaneously.

[Claim 13]A manufacturing method of a porous electrode of "claim 12", wherein a green sheet consists of an ion-conductive solid electrolyte substance.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention is used for a fuel cell and others, and relates to a porous electrode with suitable quick speed of response, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]Generally, since particle diameter made it come to distribute around 12-micrometer metal powder in a vehicle, conductive paste could not become becoming the thickness over 10 micrometers, and homogeneous continuation porosity easily, when it was going to form the porous electrode, and became a very bad thing of the response.
[0003]
[Problem(s) to be Solved by the Invention]Therefore, if over [of the paste / reverse side] is carried out, and it applies thinly and calcinates as a paste of the diameter of a granule in order to obtain a thin electrode with a sufficient response, the electrode would lose continuity and the electrical continuity of it will have been lost. The degree will become large when it calcinates by a 1500 degreeC grade, since especially the endurance of an electrode is increased. Then, an object of this invention is to provide the porous electrode of thin homogeneous continuation stoma nature.
[0004]
[Means for Solving the Problem]The purpose of this invention that in which particle diameter carried out mixture dispersion for the end of ceramic powder, as for said platinum metal powder, particle diameter differs [particle diameter] from platinum metal powder of 1 micrometer or less at 1 micrometer or less, It is attained by porous electrode which gives a paste which it makes it come to distribute in a vehicle to a substrate by printing, spreading, or other means, and is calcinated. The purpose of this invention is attained by porous electrode of "claim 1" whose platinum metal powder is platinum powder. The purpose of this invention is

attained by porous electrode of "claim 1" whose platinum metal powder is platinum-rhodium alloy powder. The purpose of this invention is attained by porous electrode of "claim 1" which is 15 or less mass percents of platinum metal powder the end of ceramic powder. The purpose of this invention is attained by porous electrode of "claim 1" which it is in the end of gas permeation nature ceramic powder the end of ceramic powder. The purpose of this invention is attained by porous electrode of "claim 5" which is the refining zirconia powder which reformed some zirconia powder so that oxygen transmittance might be increased a porous electrode of "claim 5" which is zirconia powder the end of gas permeation nature ceramic powder, or the end of gas permeation nature ceramic powder. The purpose of this invention is attained by one porous electrode of "claim 1" to "claims 7" whose particle diameter of both sides of platinum metal powder and the end of ceramic powder is 0.1 micrometer or less. Since the purpose of this invention carries out mixture dispersion of platinum metal powder and the end of ceramic powder with a dry type ball mill, make it distribute in a vehicle and it obtains a paste, a manufacturing method of a porous electrode which gives said paste on a substrate and calcinates it after an appropriate time -- or, Since ultrasonic mixture dispersion of platinum metal impalpable powder and the ceramic impalpable powder is carried out underwater, dry, and make it distribute in a vehicle, and a paste is obtained, A manufacturing method of a porous electrode which gives said paste on a substrate and calcinates it after an appropriate time, Or after carrying out ultrasonic mixture dispersion of platinum metal impalpable powder and the ceramic impalpable powder underwater and drying, what carried out re-mixture dispersion with a dry type ball mill is distributed in a vehicle, and a paste is obtained, and it is attained by a manufacturing method of a porous electrode which gives said paste on a substrate and calcinates it after an appropriate time. A manufacturing method of one porous electrode of "claim 9" to "claims 11" in which the purpose of this invention is characterized by a substrate's consisting of green sheets and calcinating a substrate and a porous electrode simultaneously, Or a green sheet is attained by a manufacturing method of a porous electrode of "claim 12" consisting of an ion-conductive solid electrolyte substance.

[0006]

[Embodiment of the Invention]According to this invention, an about 3-micrometer thin electrode can be formed by the particle diameter of platinum metal powder and the end of ceramic powder being 1 micrometer or less. In order to join together so that the particles of different particle diameter by changing the particle diameter of platinum metal powder and the end of ceramic powder, and carrying out mixture dispersion may make surface free energy small, Particles distribute in the state of certainly accomplishing a pair, and form the porous electrode of homogeneous continuation stoma nature in the state of sintering in a platinum metal powder particle and the end of ceramic powder. Under the present circumstances, if the end of ceramic powder is made into 15 or less mass percents of platinum metal powder, the

conductivity of a porous electrode is maintainable. Since the gas stability of material will be good and will be a low melting point comparatively as platinum metal powder if platinum powder or platinum-rhodium alloy powder is used, the calcination work at the time of forming a porous electrode becomes easy in comparison. If the end of ceramic powder some porous electrodes are formed is used as the zirconia powder of end of gas permeation nature ceramic powder, for example, oxygen, permeability, etc., if it shall become a good electrode of a reaction with the fuel gas of a fuel cell, etc. and the particle diameter of platinum metal powder and the end of ceramic powder shall be 0.1 micrometer or less, electrolyte thickness becomes thin, and the speed of response of an electrode will be markedly alike, and will improve.

[0007]By carrying out mixture dispersion of the platinum metal powder which differs in particle diameter, and the end of ceramic powder within [both] a dry type ball mill, a mechanochemical effect is added to both powder and the platinum metal powder which differs in particle diameter, respectively, and the end of ceramic powder distribute to pair shape. When material is impalpable powder, mixture dispersion can be suitably carried out with an ultrasonic wave. If a green sheet is used as a substrate, an arbitrary-shaped porous electrode can be provided, and a substrate portion can also be made into gas permeation nature if it is considered as a further ion-conductive green sheet.

[0008]

[Example 1] The zirconia powder reformed so that mean particle diameter might carry out yttrium processing of the platinum powder with a mean particle diameter of 0.05 micrometer in calcium handling at 0.16 micrometer with 100 weight sections and oxygen transmittance might be increased was fed into the planet type ball mill, and dry-blending distribution of the ten weight sections was carried out for 6 hours. The mixture dispersion powder obtained here was distributed in the vehicle which consists of resin, a solvent, a surface-active agent, etc., and the paste was obtained. Thus, by mixing beforehand the platinum metal powder (platinum powder) and the end of ceramic powder (zirconia powder) particle diameter differs with a ball mill, Since it joins together and suits so that the particles from which particle diameter differs may make surface energy small, and also the physical force by the collision of a ball is added and also a mechanochemical effect is also added, it distributes, after a powder comrade from whom particle diameter differs joined together and there has been. That is, since particle diameter differs, it is lost that a comrade condenses in a platinum metal powder comrade or the end of ceramic powder. As a result, it will distribute in the state where it always adjoined each other during the paste platinum metal powder and the end of ceramic powder. The 1.8-micrometer-thick porous electrode was obtained by giving the paste obtained in this way on the green sheet which consists of an ion-conductive solid electrolyte substance, and calcinating it by 1500 degreeC. In evaluation of this porous electrode, speed of response can be known by alternating-current-impedance measurement, and has correlation of [response time

and positive] in the product (RxC= damping time constant) of the resistance R and the capacitance C which are obtained by alternating-current-impedance measurement. A four point probe method etc. can estimate a conductor resistance value. Then, the place and damping time constant which placed the porous electrode into the oxygen current of 600 degreeC, impressed the voltage of 0.01 volt, and performed impedance measurement were 0.043 second. Conductor resistance values were 418mohm/**. The obtained porous electrode was perfect continuation stoma nature.

[0009]

[Example 2] After supplying platinum powder 100 weight section with a mean particle diameter of 0.05 micrometer and zirconia powder 10 weight section with a mean particle diameter of 0.1 micrometer to the planet type ball mill and carrying out dry-blending distribution for 6 hours, it was made to distribute in a vehicle and the paste was obtained. The 1.6-micrometer-thick porous electrode was obtained by giving this paste on the green sheet which consists of an ion-conductive solid electrolyte substance, and calcinating it by 1500 degreeC. The obtained porous electrode is perfect continuation stoma nature.

The damping time constant was 0.015 second and conductor resistance values were 220mohm/**.

[0010]

[Example 3] After supplying platinum powder 100 weight section with a mean particle diameter of 0.05 micrometer and zirconia powder 10 weight section with a mean particle diameter of 0.35 micrometer to the planet type ball mill and carrying out dry-blending distribution for 6 hours, it was made to distribute in a vehicle and the paste was obtained. The obtained paste was applied on the substrate, and was given, it calcinated by 1500 degreeC, and the 2.0-micrometer-thick porous electrode was obtained. This porous electrode is perfect continuation stoma nature as a result of evaluation.

The damping time constant was 0.030 second and conductor resistance values were 180mohm/**.

[0011]

[Example 4] Platinum powder 100 weight section with a mean particle diameter of 0.05 micrometer and zirconia powder 10 weight section with a mean particle diameter of 0.02 micrometer are supplied in a tank, Since supersonic vibration is given into this tank and mixture dispersion of both the powder was carried out, this distributed powder is dipped up with the net of the suitable diameter of a pass hole, etc., and was dried, the end of dry matter dusting platinum powder and zirconia powder carried out equivalent distribution was distributed in the vehicle, and the paste was obtained. After giving the obtained paste on the green sheet

which is uncalcinated ****, both were calcinated by 1500 degreeC and the 2.0-micrometer-thick porous electrode was produced to calcination ****** which forms a substrate. The platinum powder and zirconia powder which were highly distributed by supersonic vibration formed the porous electrode of perfect continuation stoma nature by calcination as a result of evaluation, the damping time constant was 0.05 second and conductor resistance values were 390mohm/**.

[0012]

[Example 5] After adding and carrying out mixture dispersion of the supersonic vibration underwater, platinum powder 100 weight section with a mean particle diameter of 0.05 micrometer and zirconia powder 10 weight section with a mean particle diameter of 0.02 micrometer are pulled up from the water, and were dried, and dry-blending distribution of this end of dry matter dusting was carried out with the planet type ball mill for 6 hours. Then, this dry type re-mixture dispersion powder was distributed in the vehicle, and the paste was obtained. The obtained paste was given on the green sheet which consists of an ion-conductive solid electrolyte substance, and both were calcinated by 1500 degreeC. This produced the 1.6-micrometer-thick porous electrode to calcination ****** which forms a substrate. The obtained porous electrode had a fine continuation stoma as a result of evaluation, the damping time constant was 0.02 second and conductor resistance values were 150mohm/**.

[0013]

[Comparative example 1] Platinum powder 100 weight section with a mean particle diameter of 1.0 micrometer and zirconia powder 10 weight section with a mean particle diameter of 0.14 micrometer, After applying on the substrate the paste obtained by distributing in a vehicle and giving it, the place and porous electrode which calcinated by 1500 degreeC and produced the 3.0-micrometer-thick porous electrode were divided in some places, continuity was lost, and electrical continuity was not obtained. Since mixture dispersion of platinum powder and the zirconia powder was carried out beforehand and it was not made to distribute like this invention so that platinum powder and zirconia powder may certainly accomplish a pair, this is because it was dotted with a platinum powder comrade's condensation portion, or the zirconia powder comrade's condensation portion.

[0014]

[Comparative example 2] Platinum powder 100 weight section with a mean particle diameter of 0.05 micrometer and zirconia powder with a mean particle diameter of 0.14 micrometer are fed into a planet type ball mill, dry-blending distribution was carried out for 6 hours, this mixture dispersion powder was distributed in the vehicle, and the paste was obtained. The obtained paste was applied on the substrate, and was given, this was calcinated by 1500 degreeC, and the porous electrode of 4.0-micrometer thickness was produced. However, although the

porous electrode shape of continuation stoma nature was obtained, since there was too much content of zirconia powder and the platinum particle comrade's consecutive contact was not obtained, electrical continuity was not obtained.

[0015]In the above-mentioned example, although the example of platinum powder was shown as an example of platinum metal powder, after alloy powder, such as powder, such as a ruthenium, rhodium, palladium, osmium, and iridium, or a platinum-rhodium alloy, can be used. Although the example of the zirconia powder of oxygen permeability was shown as ceramics of gas permeation nature, in addition to this as ceramics of oxygen permeability, oxide ceramics, such as alumina and cerium, can be used. Of course, depending on a use, hydrogen permeability ceramics, the ceramics of nitrogen permeability, etc. can be used. Although the manufacturing method by an ultrasonic mixture dispersion method is suitable for the mixture dispersion of impalpable powder, in order to compensate the adverse effect by sedimentation of the impalpable powder after a vibrating stop, etc., it can repeat the mixture dispersion by a dry type ball mill again after powder desiccation.

[0016]

[Effect of the Invention]According to [above-mentioned passage] this invention, a 3 micrometers or less-thick continuation stoma nature porous electrode can be obtained with sufficient reproducibility, response time is short, and since a conductor resistance value is a porous body of it being not only small but continuation stoma nature, an electrode with high endurance can be provided that it is hard to damage to heat stress. In this invention, platinum metal powder is used as a conductor.

Therefore, since chemical stability serves as a strong and long-life electrode and also the material of gas permeation nature with various kinds of gas (or fuel fluid), NURE nature, or compatibility can be used as ceramics, If the electrode according to various kinds of uses shall be provided and the particle diameter of platinum metal powder and the end of ceramic powder shall be 0.1 micrometer or less, the advantage of being able to shorten response time substantially will also be acquired.

[Translation done.]